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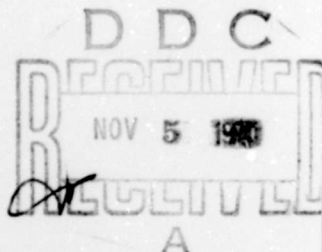
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RUBBER TOUGHENED ACRYLIC POLYMERS FOR ARMOR APPLICATIONS

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I. INTRODUCTION

A program on the mechanical and dynamic properties of rubber toughened acrylic polymers has led to advances in materials which solve two Army material problems.

The first problem is the ballistic resistance and spallation or fragmentation of window materials upon impact from fragments and/or foreign objects. This impact results in the production of many high speed particles which can and do injure the occupant of the vehicle--particularly in aircraft--even though the missile itself was on a trajectory which would not have struck the occupant. As a result of this research the spall problem has been eliminated, and through the use of a gradient rubber content a sixfold improvement in ballistic energy absorption over the unmodified acrylic polymer has been achieved.

The second problem which has been solved is the reduction in thickness of a transparent composite designed to protect against small arms fire. The reduction in thickness will have two benefits--first, for the soldier it will reduce the error in accurate target acquisition because the light will have a lesser path in which to be refracted before being received by the eye and second, this more efficient backup will permit the utilization of thinner sections of the rather expensive transparent ceramic component.

These improvements were achieved through the modification of polymethylmethacrylate (PMMA) by inclusion of rubber particles in the polymeric matrix. While it has been known for some time that the impact behavior of brittle polymers such as polystyrene can be improved by this technique (1), and while more recently the concept has been extended to acrylic polymers and to the thermosetting resins used in fiber-reinforced composites (2), until now

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the concept has not received any consideration for ballistic applications. In this investigation a series of rubber modified acrylics was examined over a range of rubber contents from zero to 16 percent with marked improvements in the ballistic resistance being obtained.

II. FRAGMENT PROTECTION AND SPALL ELIMINATION

The addition of the rubbery particles to the glassy matrix has a marked effect on the mechanical and ballistic properties of the PMMA. The tensile modulus and yield stress of these materials measured by a standard Instron test at an elongation rate of 7 percent/minute are shown in Figure 1. Both the modulus and yield stress decrease monotonically by nearly a factor of two over the range of rubber contents investigated indicating the extent of softening resulting from the addition of the rubbery particles. The ballistic resistance of these same materials against 17 grain, 22 caliber, fragment simulators is shown in Figure 2. The graph shows the ballistic resistance in terms of a V_{50} versus rubber contents for three different thicknesses or areal densities. At the lowest areal density (.093" thick) the maximum ballistic resistance occurs at 10 percent rubber content. As the thickness increases to .156", the greater rubber contents all behave in a similar fashion. At the highest areal density (.250"), however, the optimum ballistic resistance has shifted to 13 percent rubber, while the 10 percent material has a significantly lower V_{50} . Unlike the static mechanical behavior, then, where the tensile modulus and yield stress decrease monotonically, the ballistic resistance, except at very low rubber contents, improves with increasing rubber content. The optimum behavior occurs at higher rubber contents as the thickness or areal density of the material increases. As the areal density is made larger, however, the V_{50} impact velocity increases; consequently, the rate of loading is greater. It would appear, then, that the shift of the optimum ballistic energy absorption to higher rubber contents is caused by the increasing rate of loading.

Inspection of Figure 2 reveals a result extremely important from an armor standpoint. Over the range of rubber contents the ballistic limit increases by a factor of two, corresponding to a fourfold increase in the energy absorbed by the ballistic impact. Not only that but the optimum ballistic resistance of the $\frac{1}{4}$ inch material ($V_{50} = 1000$ ft/sec) is 15 percent better than polycarbonate (Lexan) currently considered the best transparent fragment-resistant material.

PMMA, the material used in most helicopter windshields, and many other homogeneous polymers undergo extensive cracking and spallation when subjected to ballistic impacts presenting a serious hazard to personnel behind the material. In marked contrast, however, the rubber-modified acrylics undergo considerable stress whitening, and spallation and cracking are

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essentially eliminated. This is demonstrated in Figure 3 where there are shown photographs taken after the impact of a 17 grain fragment simulator against the acrylic materials. The impact on the left is for a partial penetration of the zero percent rubber material (PMMA). Cracking and spallation are evident; i.e., even though the missile was stopped, secondary fragments spalled from the rear of the material. The impacts shown in the center and right of Figure 3 are for a partial penetration and a complete penetration of the 16 percent rubber material. No spallation is evident for the partial penetration. Note the concentric rings of stress-whitened area. This is typical of the higher rubber content materials in this series and is indicative of a greater degree of energy absorption arising from an increased amount of craze volume formed during the impact. It has been our observation that in this rubber-modified acrylic series the greater the amount of this stress whitening, the better the material will absorb the ballistic impact energy.

In an attempt to understand the reinforcement mechanisms responsible for the improvement in ballistic resistance under impact with 17 grain fragment simulators, Scanning Electron Micrographs were taken of the penetration path through $\frac{1}{4}$ " of the 16 percent material. These are shown in Figure 4. The photograph at the left was taken at the entrance of the 17 grain missile. The smooth surface is indicative of glassy or brittle fracture. The center picture was taken in the middle of the penetration path; the roughness of the fracture surface is indicative of a transition from glassy to ductile fracture behavior. The picture on the right was taken near the exit of the missile, and the gross roughness indicates very ductile behavior. These observations suggested that improved ballistic resistance might result if a gradient in properties could be introduced in a laminate with the facing material high in modulus and glassy, and the rear material low in modulus and ductile. Accordingly, a gradient armor was fabricated by laminating sheets of progressively increasing rubber content (0%-1-4-7-10-13-16%) in a hot press and testing it ballistically both with the 0 percent facing the missile and with the 16 percent material facing the missile. The results are shown in Figure 5. The curve is for the V₅₀ of the individual rubber contents normalized to 30 ounces/sq ft. The 0-16 percent laminate gave a V₅₀ of 1295 fps, about 18 percent higher than the V₅₀ of the optimum single rubber content (1100 fps). The 16-0 percent laminate gave a V₅₀ of 960 fps, inferior to the 13 or 16 percent contents indicating that the result at 1295 fps was not a fortuitous one arising from the heat or lamination treatment. Thus, a marked improvement was obtained by grading the rubber content. This graded rubber content, besides showing better ballistic behavior than any individual rubber content, is about 35 percent better than polycarbonate. Together with the spall elimination this renders the graded rubber-modified acrylic polymer the best candidate material for future transparent armor.

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III. STATIC IMPACT AND FRACTURE SURFACE ENERGY MEASUREMENTS

In an effort to correlate the ballistic impact behavior of these materials with a common, more easily performed experiment, the Izod impact and fracture surface energy (FSE) were determined as a function of rubber content. The Izod impact was chosen to determine if the ballistic event could be simulated by a relatively static test, while the FSE measurements were made to determine if an important phenomenon involved in the ballistic event, namely the creation of new surface, could correlate with the overall ballistic performance. The results are shown in Table I. The third column in this Table shows the results of a three-point bending test (3) which is extremely easy to perform but which gives a complicated mechanical stress pattern rendering it difficult to interpret the results in a meaningful fashion. The last column in Table I gives FSE values obtained with a cleavage technique (4) using a tapered reinforced bar to obtain adequate stiffness and a constant compliance in the test specimen.

Comparing these results with the ballistic behavior (Figure 2) one can see similar trends but not an exact one-to-one correlation. The lower rubber contents have low Izod and FSE values as well as low V_{50} 's, while increasing the rubber content gives higher Izod and FSE values and better ballistic resistance. However, the ballistic results seem to be more sensitive to intermediate rubber contents than the other tests. In addition, the Izod and three-point bending FSE show the 16 percent rubber content to be superior, while the cleavage FSE shows the 10 percent rubber to be the best, and the ballistic data show 10 or 13 percent to be superior depending on the rate of loading. This discrepancy can be qualitatively explained by **realizing that the ballistic behavior is** a result of several competing mechanisms dependent on many factors (e.g., crack initiation, crack propagation, void formation, amount of craze volume, rate of loading, rubber particle size and distribution, shear effects, etc.) and cannot be simulated by a test addressing only a small number of these variables. Consequently an exact correlation between the ballistic resistance and any one other test would certainly be fortuitous.

An important factor involved in the lack of correlation between the Izod impact, FSE, and ballistic tests is the different rate of loading, shown earlier to be an important factor in determining the optimum rubber content. This effect can also be seen from the results of puncture tests shown in Figure 6. This test was performed by an instrument measuring load and displacement necessary to puncture the test specimen at a given rate of loading. At low puncture rates (20"/min.) the optimum work to puncture occurs at 10 percent rubber content, while at higher rates (11,700"/min.)

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the 13 and 16 percent appear to be superior. This is in qualitative agreement with the ballistic results shown in Figure 2 where increasing the impact velocity shifted the optimum rubber content from 10 percent to 13 percent.

IV. APPLICATION IN TRANSPARENT ARMOR COMPOSITE SYSTEMS

While it is evident that the rubber particles provide significant improvements in the ballistic resistance against fragment simulators, the question arises whether these results will translate into improved properties of bullet-resistant armor where the polymeric backup accounts for only a quarter of the total areal density. Table II shows the ballistic behavior of the rubber-modified acrylic series tested as a backup with glass for 30 cal. ball impacts. There is a large difference between the 10 percent and 13 percent rubber contents with the greatest V_{50} occurring at the 16 percent rubber. The actual optimum rubber content may be higher yet than 16 percent. Again, the effect of rate of loading appears to be quite important in determining the optimum rubber content. It is noteworthy that nearly a twofold increase in V_{50} occurs over the range of rubber contents shown, although the rubber-modified acrylic backup accounts for only 22 percent of the total areal density of the glass-acrylic laminate. This indicates that substantial improvements in bullet-resistant transparent armor over that currently available may be achieved by utilizing these rubber modified materials in their optimum configuration.

While the above results indicate that significant improvements in the ballistic resistance of glassy polymers can be achieved by toughening them with rubbery particles, the story is by no means complete. Only one variable has been treated here, the amount of rubber content. Particle size and distribution are known to be important at low speed impacts and may well be important parameters at ballistic rates of loading. These parameters will also affect and can improve the transparency and its temperature dependence of these rubber modified materials. It is the tendency of these materials to haze at lower temperatures which is the only serious drawback to their being used in armor today. Changing the particle size and distribution should eliminate this deficiency.

V. CONCLUSIONS

The concept of improving the impact resistance of acrylic polymers by toughening them by inclusion of rubbery particles into the glassy matrix can be extended to the ballistic regime. Over the range of rubber contents investigated (0-16 percent) a twofold increase in V_{50} was observed, corresponding to a fourfold improvement in energy absorption, both against 17 grain fragment simulators and against 30 cal. ball impacts where the

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rubber modified acrylic accounted for less than one quarter of the total areal density. The optimum rubber content for maximum ballistic resistance depends on the rate of loading and shifts to higher values (i.e., 10%, 13%, or 16% and higher) as the impact velocity increases. Addition of the rubber particles also eliminates spalling, a potentially serious hazard to personnel, with brittle materials such as PMMA.

The complex phenomena involved in the ballistic process cannot be adequately represented by any single test investigated. Rather, a series of tests such as work to puncture, FSE, and Izod impact, must be performed, and even then only trends in the data can be compared, not specific values.

Fracture surface electron micrographs indicated a transition from brittle to ductile fracture through the penetration path of a fragment simulator. Enhancing this phenomenon by grading the rubber content from 0 to 16 percent gave ballistic results 18 percent higher than any single rubber content and 35 percent better than Lexan, currently considered the best transparent fragment-resistant material. These results indicate that substantial improvements in transparent armor can be achieved by optimizing both the rubber content and its gradient for a particular application and utilizing these rubber modified materials in future armor systems.

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UNCLASSIFIEDTABLE IIZOD IMPACT AND FRACTURE SURFACE ENERGY OF RUBBER
MODIFIED PMMA

<u>Rubber Content %</u>	<u>Izod Impact (ft-lb/inch)</u>	<u>Three Point Bending FSE (ergs/sq cm)</u>	<u>Cleavage FSE (ergs/sq cm)</u>
0	0.13		5×10^5
1	0.13	18×10^5	$37 \times "$
4	0.46	$42 \times "$	$47 \times "$
7	1.96	$53 \times "$	$82 \times "$
10	1.85	$66 \times "$	$87 \times "$
13	1.85	$64 \times "$	$77 \times "$
16	2.78	$71 \times "$	$50 \times "$

TABLE IIBALLISTIC BEHAVIOR OF GLASS-RUBBER MODIFIED PMMA LAMINATES
(PMMA BACKUP = 22% OF TOTAL WEIGHT)

<u>Rubber Content (%)</u>	<u>V50 (30 cal. Ball) (feet per second)</u>
0	1422
1	1301
4	1223
7	1384
10	1482
13	1962
16	2240

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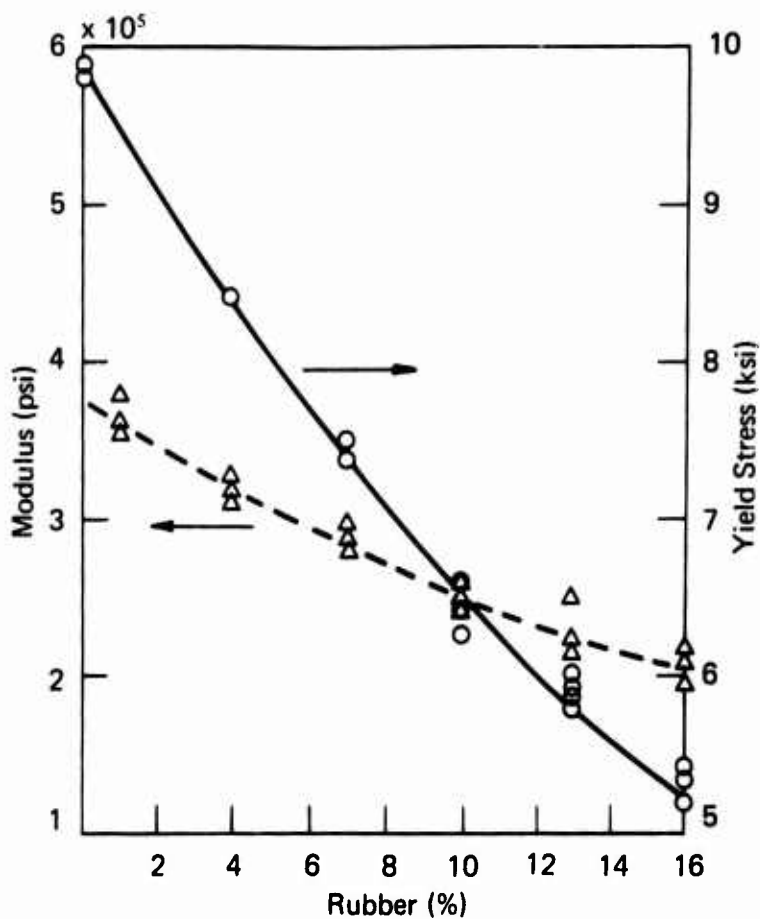


Figure 1. Tensile modulus and yield stress of rubber-modified PMMA (elongation rate = 7 percent/min)

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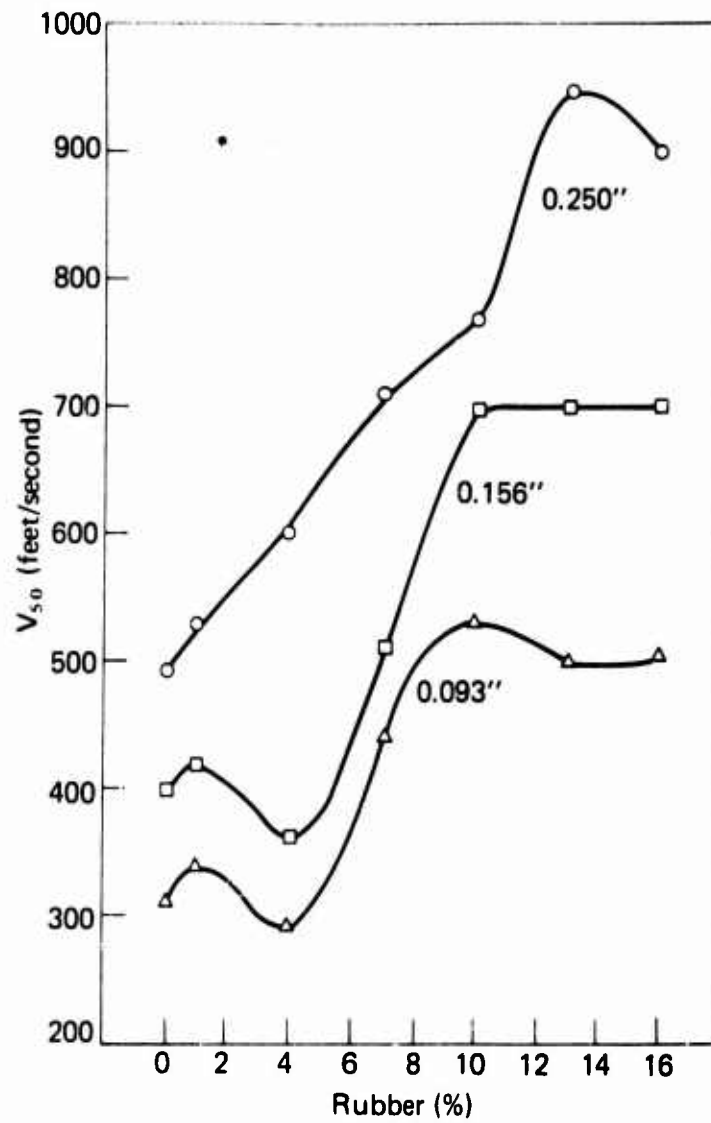


Figure 2. V_{50} ballistic limit of rubber-modified PMMA as a function of rubber content for 17-grain - 22 caliber fragment simulators

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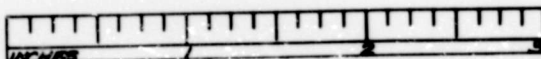
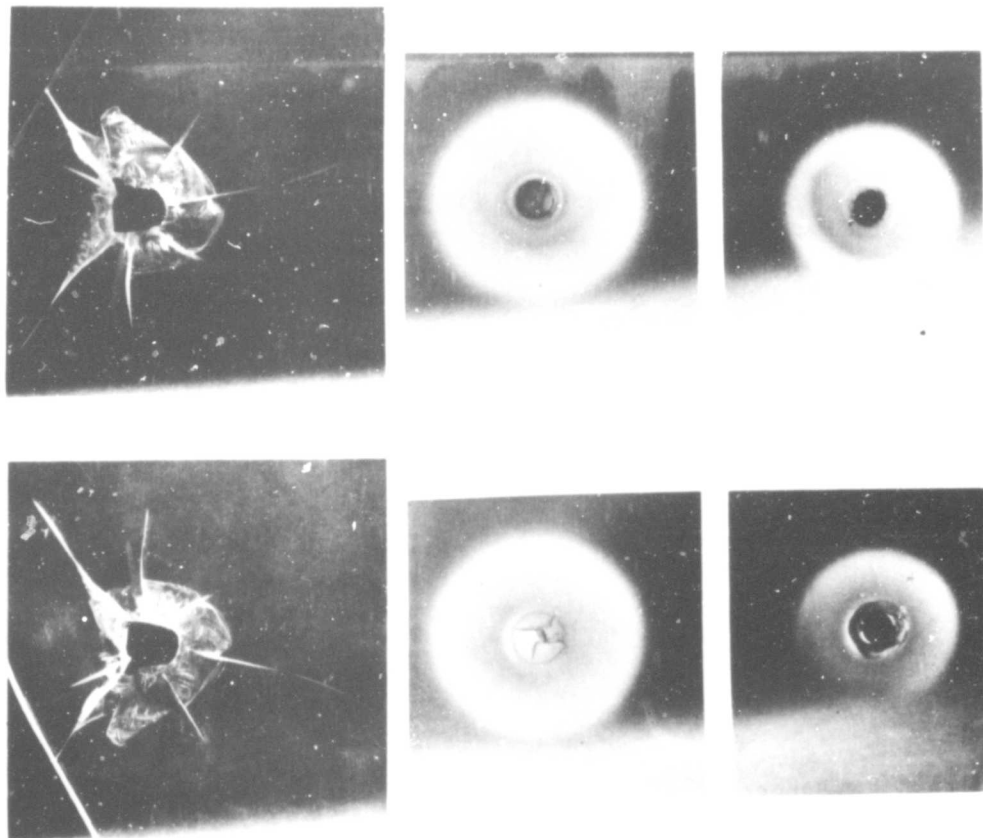


Figure 3. Ballistic impact of rubber modified PMMA with 17-grain fragment simulators. (Left) Partial penetration of zero rubber content PMMA. (Right) Complete penetration of 16 percent rubber-modified PMMA. (Center) Partial penetration of 16 percent rubber-modified PMMA. Top set of photographs is facing impacting missile; bottom set is of the rear of the impact.

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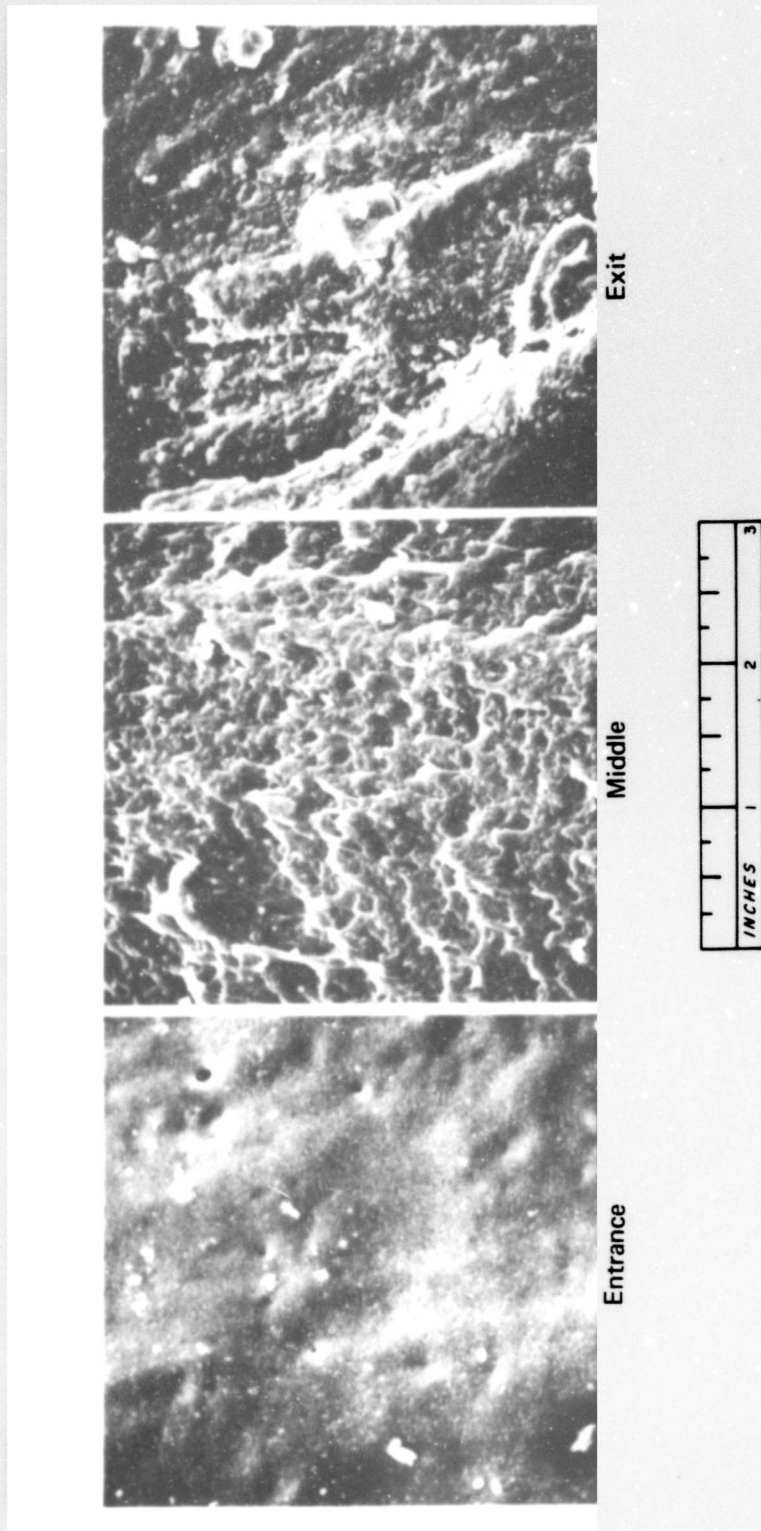


Figure 4. Scanning electron micrographs of fracture surface produced by penetration of 16% rubber-modified PMMA (0.250") by a 17 grain - 22 caliber fragment simulator.

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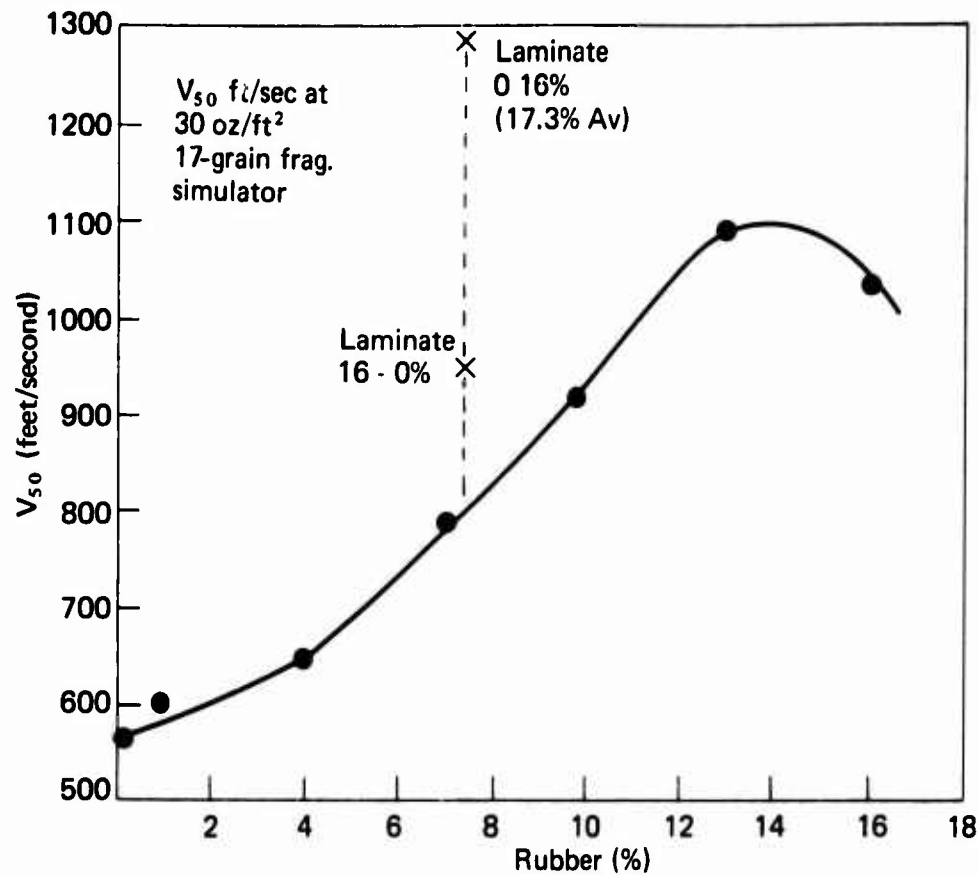


Figure 5. V_{50} ballistic limit of rubber modified PMMA and gradient laminates as a function of rubber content for 17-grain - 22 caliber fragment simulators

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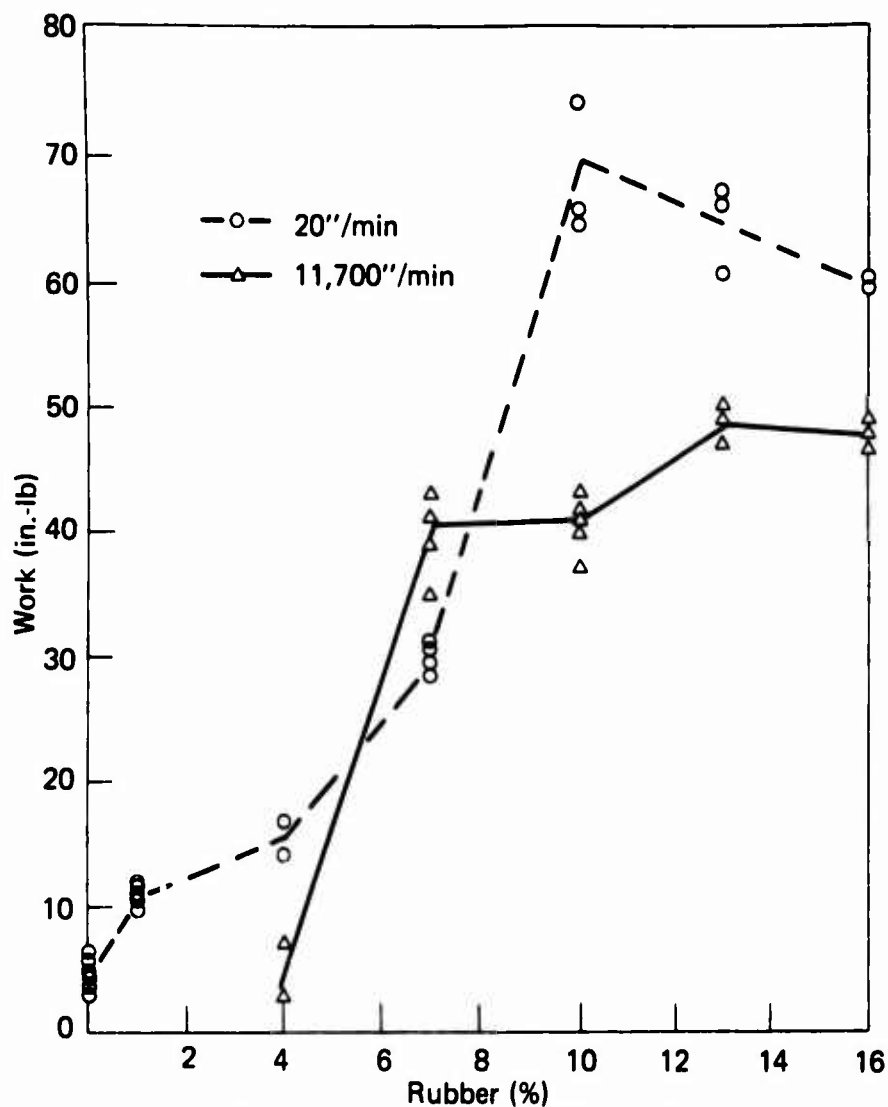


Figure 6. Work to puncture at low (20 in./minute) and high (11,700 in./minute) rate as a function of rubber content